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Processing Use, and Characterization of Shale Oil Products

by Andrew W. Decora* and Robert D. Kerr†

Oil shale is a potential source of oil that will supplement conventional sources for oil as our needs for fossil fuels begin to exceed our supplies. The resource may be mined and processed on the surface or it may be processed *in situ*. An overview of the potential technologies and environmental issues is presented.

Introduction

The need for energy for domestic and commercial purposes is world-wide and rapidly increasing. In most parts of the world, the most critically needed forms of energy are hydrocarbons, which are the source for motor fuels needed for transportation and for the easily transportable high energy gases used for domestic purposes and for power generation. The widespread occurrence of organic-containing rocks, or oil shales, throughout the world make this material a possible substitute particularly for petroleum and natural gas as sources of fossil energy.

Two general alternatives are available for utilization of oil shale: the first is to burn the shale directly as fuel and the second is to convert it to some other form of fossil energy. Direct combustion offers the simplest and least expensive approach to the utilization of oil shale. The second alternative requires conversion of oil shale to liquid or gaseous products. In the United States, utilization of oil shale has been considered almost entirely as a substitute for natural petroleum and gas, and, consequently, this paper will consider mostly technologies directed towards these end products.

The potential oil shale resource in the United States is large. Although oil shale occurs in 30 states, the richest deposits are concentrated in the Green River formation in Colorado, Utah, and Wyoming (Fig. 1). On a basis of estimated total oil in place, the 1.8×10^{12} barrels in this formation represent 82% of the 2.2×10^{12} barrels in the United States. The Green River formation underlies about 25,000 square miles of semi-arid, sparsely populated land at an elevation of 5000 to 8000 ft. Of this area, about two-thirds is thought to be commercially developable in the foreseeable future. The richest regions in the formation are in the Piceance Creek (Colorado), Uinta (Utah), and Green River (Wyoming) Basins.

The formation is up to 1800 to 3500 ft thick in places, under an overburden of 1000 to 3000 ft. Although yields vary from insignificant volumes to about 105 gal. (2.5 barrels) oil/ton of shale, the usual range in the more commercially interesting regions is 15 to 35 gal. raw oil/ton of shale (a yielding of 33 gallons of raw oil is considered relatively rich). In the central portion of the Piceance Basin, a 2000-ft bed that underlies about 1000 to 2000 ft barren overburden should produce an average of 25 gal. (0.6 barrel) oil/ton of shale.

Approximately one-third of the Green River formation oil, or about 600×10^9 barrels, is in beds at least 10 ft thick that assay 0.6 barrel or more per ton of shale, an amount about two-thirds larger than the 1972 proved Middle East oil reserves of 355×10^9 barrels. If 5% of the Green River formation proves suitable for near-term development, the equivalent shale oil reserve is 90×10^9 barrels. This vast quantity of oil could substantially ameliorate the national energy situation.

Over the years a number of studies have been made to extract the organic material from oil shales. The only practical technology that has been developed is the use of high temperatures, approximately 900°F (480°C), to retort or decompose the solid organic material by pyrolysis. The shale can be heated by direct or indirect methods. Utilization of solvents to remove the organic materials from oil shales has not been successful.

* Department of Energy, Laramie Energy Technology Center, P. O. Box 3395, University Station, Laramie, Wyoming 82071.
† Deceased.

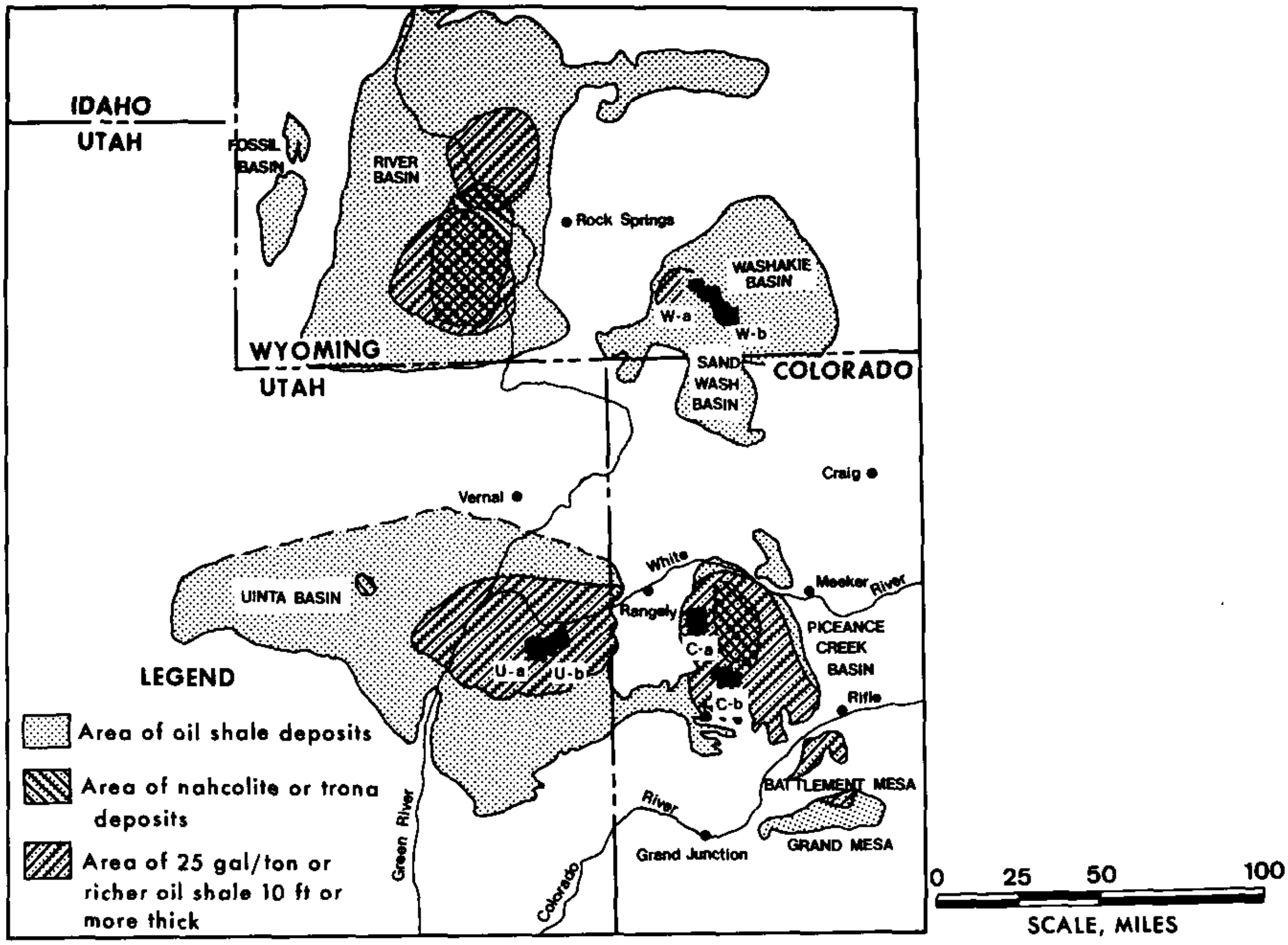

FIGURE 1. Oil shale areas, Colorado, Utah, and Wyoming. The map shows the location of the six tracts of oil shale lands that were offered for sale under the Prototype Oil Shale Leasing Program. These tracts are designated: C-a, C-b, U-a, U-b, W-a, and W-b. Of these, tracts W-a and W-b failed to attract industrial interest and were not leased.

Retorting can be accomplished aboveground in retorting equipment. This method has been relatively well developed and operations have been conducted at modest levels. Retorting can also be accomplished underground by a number of true or modified *in situ* processing methods. Heating the oil shale can be accomplished by internal combustion, by circulating hot fluids, or by circulating hot solids. Figure 2 is a diagrammatic representation of the possible processing methods for oil shales. These methods will be discussed individually in the sections to follow.

History of Processing

Commercial interest in the extraction and processing of oil shale has been shown for several decades. A viable oil shale industry has been contemplated several times in the past 25 to 30 years, but each time numerous roadblocks have postponed actual development. More recently, the impetus to develop domestic energy sources has prompted many new government and privately sponsored oil shale activities. This apparent increased interest in oil shale has also led to increased concern about environmental impacts which might be associated with large-scale extraction and processing operations.

Mining and Surface Retorting

The greatest amount of actual experience in mining oil shale has involved underground mining techniques. An underground mining method for oil shale has been developed and demonstrated by the U. S. Government and industry at the Anvil Point research facilities near Rifle, Colorado. The mine was opened in the Mahogany zone to demonstrate the

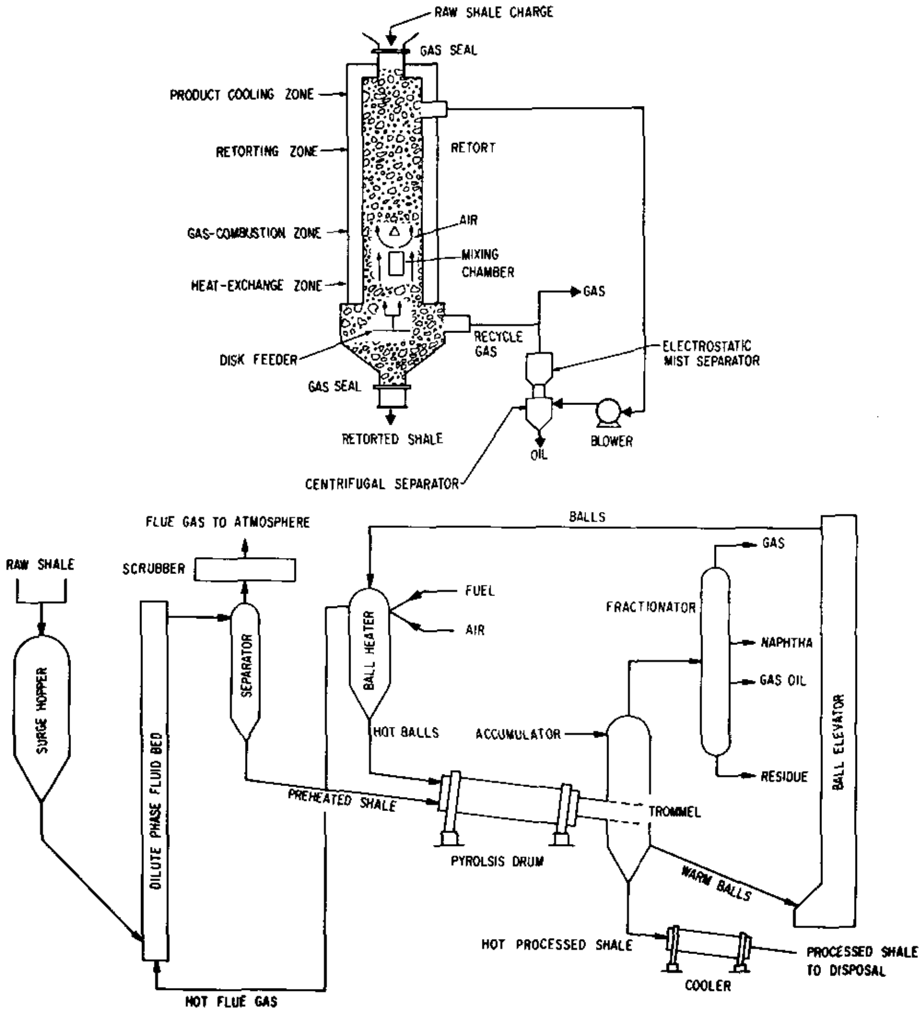

FIGURE 2. Schematic representations of (top) the gas-combustion and (bottom) the TOSCO retorting process. In gas-combustion retorting, recycle gas is mixed with air and burned within the retort. Gases flow upward and shale moves downward. In the TOSCO retort, ceramic balls transfer heat to the shale. No combustion takes place in the retort.

feasibility of room-and-pillar mining methods, to develop and test equipment, and to determine whether low mining costs and high recovery were possible. Major work in underground mining continues.

No open-pit mining of United States oil shale deposits has ever been done; however, this method has been proposed for oil shale lease tracts in the Piceance Basin. It would provide nearly 100% recovery of all oil shale resources, in contrast to lesser recovery for known underground mining methods.

In Situ Processing

The Laramie Energy Research Center (originally U. S. Bureau of Mines and now ERDA) initiated research on liquid fuels from oil shale as a result of the Synthetic Fuels Act of 1944. For 15 years, this research was primarily concerned with oil shale physical and chemical characteristics and the properties of the shale oil resulting from surface retorting processes.

In 1959, research and development efforts were introduced on *in situ* shale oil recovery. The *in situ* investigations became a primary objective of the LERC oil shale research and have continued as a principal activity since these laboratories became the Laramie Energy Research Center of the Energy Research and Development Administration (LERC/ERDA) in 1975.

In situ research on the western U. S. oil shales in Colorado was initiated by private industry. The Sinclair Oil and Gas Company conducted field studies in the rather shallow oil shales (up to 300 ft deep) on the southern rim (Haystack Mountain) of Colorado's Piceance Creek Basin. An oil of 31° API gravity, 20°C (35°F) pour point oil was produced. In 1965, Sinclair continued field experiments in the deep shales on the northern Piceance Creek Basin.

Between 1965 and 1967, Equity Oil conducted field experiments in a naturally fractured shale zone 1000 ft deep in the center of the Piceance Creek Basin, using circulating hot methane gase. A −29°C (−20°F) pour point oil was produced, but methane loss was excessive. This project will be resumed in 1977 with joint sponsorship of ERDA through the *in situ* program of joint ERDA/industry research.

Within the past 10 years, *in situ* field experiments by industry have also been conducted in the Piceance Basin by Mobil Oil, Humble Oil, and Shell Oil Company.

In 1972, Occidental Oil Shale, Inc., began investigation of its modified vertical *in situ* process at a site near Debeque, Colorado, on the southern rim of the Piceance Creek Basin. The process involves underground mining of 20% of shale or barren rock to create void space, followed by chemical explosive rubblization and batch retorting. Underground room No. 4, a commercial-size retort some 120 ft square and 280 ft high was ignited December 1975. A fifth retort of similar dimensions is in final preparation.

Details of Processing

Many retorting processes for oil shale have been patented in the last half century, and new patents continue to be issued. Only a few processes, however, are generally considered to be prime candidates for early commercial use in first generation retorting plants. All retorting processes have one fundamental characteristic in common: the shale is heated to at least the pyrolysis temperature, which ranges from 800 to 1000°F. Although the major pyrolysis product is oil, both gas and carbonaceous residue also are formed.

Batteries of individual retorts having capacities of about 10,000 tons/day generally are visualized as an appropriate size for the commercial retorting facilities. A practical approach to scaling-up to such a size in this new field of technology involves working out solutions to engineering problems in a series of progressively larger experimental plants, the final size usually referred to as a modular single unit.

The principal mechanical features of several retorting processes are discussed as follows: The retort developed by the Union Oil Company of California operates on a downward gas-flow principle, and the shale is moved upward by a unique charging mechanism usually referred to as a rock pump. Heat is supplied by combustion of the organic matter remaining on the retorted shale and is transferred to the oil shale by direct gas-to-solids exchange. The oil is condensed on the cool, incoming shale and flows to an outlet at the bottom of the retort.

The Colony Development Corporation operated a research facility in the mid 1960's with a "semiworks" plant using the TOSCO II retort which is a rotary-type kiln utilizing ceramic balls heated in external equipment to accomplish retorting. Shale feed of −0.5 in. in size is preheated and pneumatically conveyed through a vertical pipe by flue gases from the ball heating furnace. The preheated shale then enters the rotary retorting kiln with the heated pellets, where it is brought to a retorting temperature of 900°F by conductive and radiant heat exchange with the balls. Passage of the kiln discharge over a trommel screen permits recovery of the balls from the spent shale for reheating and recycling.

Of the numerous retorts studied in the earlier Bureau of Mines program and continuing by Development Engineering at Anvil Points, the gas-combustion retort gave most promising results. This retort is a vertical, refractory-lined vessel through which crushed shale moves downward by gravity. Recycled gases enter the bottom of the retort and are heated by the hot retorted shale as they pass upward through the vessel. Air is injected into the retort at a point approximately one-third of the way up from the bottom and is mixed with the rising, hot recycled gases. Combustion of the gases and some residual carbon from the spent shale heats the raw shale immediately above the combustion zone to retorting temperature. Oil vapors and gases are cooled by the incoming shale and leave the top of the retort as a mist. The novel manner in which retorting, combustion, heat exchange, and product recovery are carried out give high retorting and thermal efficiencies.

Beyond having a common heating requirement, retorting processes also require provision for effective recovery and separation of the oil and gas products. Typically, this procedure involves transfer of the mixed product via a piping system to a closed train of commonly available equipment such as impingement-type separators, centrifugal separators, and electrostatic precipitators.

Crude shale oils produced from surface retorts may be classed generally as low-gravity, moderate-sulfur, high-nitrogen oils by petroleum standards. These are more viscous and have higher pour points (congealing temperature) characteristically than many petroleum crudes. Oils from the different processes will vary within the ranges listed in Table 1.

Table 1. Characteristics of crude shale oils.

Characteristic	Range
Gravity, °API	19–28
Sulfur, wt %	0.7–0.8
Nitrogen, wt %	1.7–2.2
Pour point, °F	80–90
Viscosity, SSU at 100°F	120–256

Gas produced from internal-combustion retorts has a low heating value of the order of 80 to 100 BTU/standard cubic foot (scf) and cannot be economically transported a substantial distance and must be utilized in the plant vicinity. Use of the higher value heating gas from the indirect-heated retort would be less limited. After treatment to remove sulfur compounds, this gas could be readily used in the plant as fuel.

In situ extraction of oil from shale is the alternative to conventional surface retorting procedures, but it is still in the early stages of development. It may be accomplished by passing retorting gases and produced liquids either vertically or horizontally through fractured shale. Application of the vertical retorting system requires a method for obtaining a cavity filled with broken shale.

The horizontal sweep approach is somewhat similar to thermal recovery methods in petroleum reservoirs. However, since oil shale deposits frequently have very low permeability, creating the appropriate fractures is a primary requirement. Applications of this general concept have been attempted at various times during the past 20 years.

Three major *in situ* research projects are now in progress, one by the Laramie Energy Research Center (ERDA) and the others by Occidental Oil Shale Corporation and Geokinetics Oil Shale Group. The LERC program involves laboratory studies, pilot-scale simulation of underground operations, and field experiments. In the field experiments near Rock Springs, Wyoming, several methods of fracturing (hydraulic pressure and chemical explosives) are being tested on an oil shale bed that is 20 to 40 ft thick and under 300 to 400 ft of overburden. Using hydraulic pressure, four horizontal fractures have been produced over a vertical interval of about 35 ft at a depth of approximately 400 ft; tests indicate that these fractures extend at least 200 ft from the injection well. Chemical explosives have also been used (in the liquid form) for detonation after being forced into naturally occurring or artificially created fractures.

The combination of hydraulic pressure and liquid chemical explosive was used for a test of *in situ* processing of shale in a formation less than 100 ft beneath the surface. Fracturing was completed in a small five-spot pattern, and the shale was then ignited for a combustion test in which about 100 barrels of oil were produced. Preparations for a similar but larger underground recovery test are in progress.

The Oxy process utilizes a combined mining and explosive fracturing technique to prepare the oil shale for *in situ* processing. In this approach, some shale is mined out from an area and adjacent shale is blasted into the mined area to create void volume. The broken shale in the room is then retorted from the top down. The present field experiment on the southwestern edge of the Piceance Creek Basin was started several years ago.

Two major problems encountered in *in situ* research to date have been (1) insufficient naturally occurring permeability for failure to induce artificially premeability so as to allow passage of gases and liquids, and (2) inability to control remotely the process with sufficient accuracy through well bores from the surface. Besides surface well bores, other methods proposed for introducing heat underground include mine shafts, tunnels, and fractures created by a variety of techniques.

In summary, a commercial *in situ* processing system has not been demonstrated to date, but a number of field-scale experiments have been conducted by government and industry during the past 20 years involving well bores from the surface. It is obvious that considerable further improvements in technology are still required before industrial-scale *in situ* recovery of shale oil could become a reality. Available information suggest that oils from *in situ* retorting may be somewhat different in quality to those produced from surface retorting. Specifically, they appear to have lower pour points, viscosities, and nitrogen contents. This is illustrated by the data in Table 2, compared to the data previously presented. *In situ* oil may be marginally suitable for transporting without upgrading because of the low pour point; however, no firm conclusions are possible because of insufficient data.

The third active *in situ* research project is being conducted by the Geokinetics Oil Shale Group in Utah. Their main processing scheme includes the utilization of horizontal retorting designs in shallow (low overburden) oil shale deposits. The porosity is

Table 2. Characteristics of oils from *in situ* retorting.

Characteristic	Range
Gravity, °API	30.6–54.2
Sulfur, wt %	0.6–1.2
Nitrogen, wt %	0.35–1.35
Pour point, °F	−15–+35
Viscosity, SSU at 100°F	40–100

provided by conventional explosives used to displace the ground surface and the shale beds.

Environmental Considerations

Oil shale development will produce both direct and indirect changes in the environment. Many of these changes will be of local significance, and others will be of an expanding nature and have cumulative impact. These major regional changes will conflict with uses of the other physical resources of the areas involved. Changes will occur to the land surfaces, water resources, air quality, wildlife habitats, aesthetic values, and existing social and economic patterns.

A major impact on the land itself will involve disposal of the retorted shale. The present emphasis on *in situ* processing is partly because this technique would obviate the necessity of disposing of large quantities of this processed shale.

Two options have been considered for processed shale disposal: (1) surface or (2) underground. Some portion of the Green River deposit appears to be most amenable to mining and surface processing. For this reason, and because of the unresolved technical problems confronting *in situ* processing, both industry and LERC are investigating problems associated with disposal of retorted shale. As disposal sites are developed in the processed shale placement operation, revegetation will begin at the first opportunity.

Revegetation research has been completed to show that spent shale from several processes will support vegetation. Research continues to develop various combinations of topsoil and mixing soil.

The potential water problems may be divided into two broad categories: nonpotable water treatment or disposal and consumptive water needs. The retorting of oil shale produces water from the combustion of fuel used to heat the shale and from decomposition of the organic matter in the shale. Because these retorting waters have been in contact with shale oil, they contain substantial amounts of organic materials in addition to the usual inorganic compounds. Experiments to treat water from gas-combustion retorting and from *in situ* retorting indicate that nearly complete removal of inorganic ions can be achieved from the retort water.

It is estimated that as much as three barrels of water are consumed for every barrel of oil produced. An operation producing 100,000 barrels of oil per day will require 12,000 to 18,000 acre-ft of water per year. Although hydrologic conditions vary both laterally and vertically, as much as 18,000 acre-ft per year may be produced in dewatering a mine for an operation producing 100,000 barrels of oil per day. This water may be used to meet processing needs.

Development of oil shale will create many direct and indirect effects to the environment in which people live. The magnitude of the effects will depend on the degree and rate of development.

The predominantly rural oil shale region will be changed with oil shale development. Changes will occur not only in the physical environment but also in the community structures and organizations, in the economic and political systems of the area, and people involved.

Each technology and activity will have associated with it certain waste streams and environmental issues. The major issues can be divided into three general sections as follows: atmospheric emission, process water and wastewater, and solids.

Atmospheric emissions can arise from several activities and operations. Of major concerns in atmospheric emissions are the potential criteria pollutants such as SO_2 (sulfur dioxide), NO_x (nitrogen oxides), CO (carbon monoxide), and HC (unburned hydrocarbons). Also of concern would be potential noncriteria pollutants such as silica, trace elements, trace organics, H_2S, CS_2, COS, and metals such as Ni, Cr, and Fe.

The above atmospheric emissions would be generated at all phases of processing due to blasting, equipment use, crushing, shale retorting, heating of gases for recycle, cleanup systems, and upgrading. Quantitative and semiquantitative emissions data are now available for several of the oil shale technologies.

Water and wastewater processing research is an important part of the overall environmental research associated with the processing of oil shale. Water is a direct product of oil shale retorting, resulting from pyrolysis of kerogen and combustion of organic material in shale. Water can be separated from the crude shale oil, can be condensed during cooling or gas cleanup, or can appear in the flue gas stream. Water separated from crude oil shale oil will contain mainly carbonate and bicarbonates, sodium, sulfate, organic acids, hydrocarbons, and ammonia. Smaller quantities of calcium, magnesium, sulfides, and trace elements may also be present. Condensed water primarily contains carbonates, traces of organic substances and sulfur containing compounds.

Wastewaters from total operations will include: oily cooling water, process water, and wash water.

For total water management considerations, most processing plans will show zero discharge of their wastewater. Reasons for total reuse of water include scarcity of water in the oil shale areas, compliance with pollution control regulations on water discharged to surface and ground water sources, and needs of the in-plant processing.

Solid wastes associated with oil shale processing are diverse and derived from all phases of processing, including mining, crushing, retorting, and upgrading. Major solid wastes of concern are retorted shale, raw shale fines, spent catalysts, activated carbon, elemental sulfur, flocculants, and calcium sulfate. Many of the secondary questions associated with the placement and disposal of the solids wastes are also of major concern. For example, retorted shale may contain solid organic residues that would be leached from the shale, inorganic salt leaching may also occur under field conditions depending on such factors as amount of available water and the manner in which the waste material is generated and disposed of.

Occupational and health effects studies are continuing with the various emissions from this processing research to determine what the long term effects will be. More importantly, evaluation of the exposure risks at the early phases of development is one of our major efforts.

The environmental impact assessments and environmental research plans are designed to generate the required data and to permit evaluations as appropriate to address the environmental issues associated later on during the process development phases.